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Easily degradable molded article and method for producing the same

[Claims]

[Claim 1] An easily degradable molding formed from a composition comprising a starch polymer, water and a thermoplastic resin, wherein the content of the starch polymer in the composition is 5-80 wt%, said starch polymer is a modified starch polymer obtained from raw starch and/or modified raw starch, and the surface of the molding of this composition is covered with an anti-fungi agent.

[Claim 2] The easily degradable molding according to claim 1 wherein
-the thermoplastic resin is biodegradable thermoplastic resin,
-the water content in the composition is 0.5-30 wt%,
-the biodegradable resin is saponificated ethylene – vinylacetate - copolymer,
-the modified starch polymer is modified raw starch which is chemically modified starch derivative, chemically decomposable starch, enzyme-modified starch, mechanically modified starch or their mixture, and
-the amount of coating with the anti-fungi agent is 2-40μg/cm^2 and the anti-fungi agent is a food preservative selected from sorbic acid, sorbates, ε-polylysine, allylisothiocyanate or their mixtures.

[Claim 3] A process for producing an easily degradable molding, comprising:
forming granules from a composition comprising a starch polymer, water and a thermoplastic resin, wherein the content of the starch polymer in the composition is 5-80 wt%, said starch polymer is a modified starch polymer obtained from raw starch and/or modified raw starch, and
covering the surface of the molding of this composition with an anti-fungi agent.

[Detailed explanation of the invention]

[0010]

[Field of industrial utilization]

The present invention relates to an easily degradable molding and a process of producing the same and more particularly to such molding consisting of a composition containing a starch polymer which is capable of preventing growth of fungi and capable of collapsing after use of the molding with microorganism and a process for producing the same.

[0011]

Biodegradable molding containing the conventional starch polymer has a superior function in that it is decomposed with microorganism into compost which is thereafter self-decomposed into carbon dioxide, and thus is conducive to treatment of refuse and accordingly fungi easily grow thereon. Means to preserve polysaccharides for a long period of time are known by JP63-32149 A which proposes to incorporate an anion surface active agent, and by JP63-32150 A which proposes to store at a low temperature.

[0012]

[Problem to be solved by the invention]

However, the conventional biodegradable molding has a problem of losing its entire value of utilization due to the growth of fungi and thus storage cost is huge which precluded the molding from the industrial utilization, and when a long term preservative is contained the biodegradable nature is precluded. The present inventor conducted extensive studies in order to obtain a molding which does not lose the value of utilization during storage due to growth of fungi and yet can easily decayed when discarded after utilization and has completed the present invention.

[0013]

The present invention has the following compositions.

(1) An easily degradable molding characterized in that it is formed from a composition comprising a starch polymer, water and a thermoplastic resin, wherein the content of the starch polymer in the composition is 5-80 wt%, said starch polymer is a modified starch polymer obtained from raw starch and/or modified raw starch, and the surface of the molding of this composition is covered with an anti-fungi agent.

(2) The above-described easily degradable molding wherein

-the thermoplastic resin is biodegradable thermoplastic resin,

-the water content in the composition is 0.5-30 wt%,

-the biodegradable resin is saponificated ethylene – vinylacetate - copolymer,

-the modified starch polymer is chemically modified starch derivative which is modified raw starch, chemically decomposable starch, enzyme-modified starch, mechanically modified starch or their mixture, and

-the amount of coating with the anti-fungi agent is 2-40μg/cm^2 and the anti-fungi agent is a food preservative selected from sorbic acid, sorbates, ε-polylysine, allylisothiocyanate or their mixtures.

(3) A process for producing an easily degradable molding, comprising:

forming granules from a composition comprising a starch polymer, water and a thermoplastic resin, wherein the content of the starch polymer in the composition is 5-80 wt%, said starch polymer is a modified starch polymer obtained from raw starch and/or modified raw starch, and

covering the surface of the molding of this composition with an anti-fungi agent.

[0014]

The present invention will be explained in detail in the following.

The easily degradable molding of the present invention is a composition comprising a starch polymer, water and a thermoplastic resin, characterized in that the content of the starch polymer in the composition is 5-80 wt%, said starch polymer is a modified starch polymer obtained from raw starch and/or modified raw starch, and the surface of the molding of this composition is covered with an anti-fungi agent.

[0015]

Starch polymer which may be used in the present invention is raw starch or modified starch polymer obtained by modifying raw starch. Examples of such raw starch are powders of corn starch, bracken starch, agon starch, potato starch, wheat starch, kissaba starch, sago starch, tapioca starch, sorghum starch, bean starch, lotus starch, trapae fructus starch, and sweet potato starch. The modified starch polymer is modified raw starch which is chemically modified starch derivative, chemically decomposed starch, enzyme-modified starch, mechanically modified starch or their mixture. Cited as the chemically modified starch derivative are allyletherified starch, carboxymethyletherified starch, hydroxyethyletherified starchs, hydroxypropyletherified starch, methyletherified starch, phosphor cross-linked starch, formaldehyde cross-linked starch, epichlorohydrin cross-linked starch, acrolein cross-linked starch, acetoacatate esterified starch, ethyl esterified starch, succinic esterified starch, xantogenic esterified starch, nitric esterified starch, ureaphosphoric esterified starch, and phosphoric esterified starch. Cited as chemically decomposed modified starch are dialdehyde starch, acid treated starch, hypochlorous acid treated starch. Cited as enzyme modified starch are hydrolyzed dextrin, and amylose. Cited as mechanically modified starch are α-starch, classified amylose, and wet thermally treated starch.

[0016]

The composition of the present invention is a composition containing starch polymer and the ratio of the starch polymer in the composition is 5-80 wt%, preferably 20-60 wt%. When the starch polymer is 5 wt% or more, the biodegradability is high, the size is stable and the workability is good. If the ratio of the starch polymer exceeds 80 wt%, the ratio of thermoplastic resin incorporated as a fluidity improving agent is small and the fluidity is low. The more the thermoplastic resin the better are the fluidity and the workability.

[0017]

The composition of the present invention contains water, preferably of 0.5-30 wt%, more preferably 2-15 wt%. The water content may be that contained in the

starch polymer or may be added to the composition or may be added after granulation. The water content imparts moldability and easiness of handling. The thermoplastic resin is preferably biodegradable and, as such biodegradable resin, saponificated ethylene-vinylacetate-copolymer, polycaprolactone, polylactic acid, and dicarboxyl acid-glycol reaction product may be cited.

[0018]

The saponificated ethylene- vinylacetate- copolymer is a polymer obtained by copolymerizing vinylacetate and ethylene and then partially hydrolyxing the vinylester moiety. Among them, saponificated ethylene- vinylacetate- copolymer having a molecular weight of 100-500,000 and saponification ratio of 0.01-99.99 %, more particularly those having ethylene content of 20-60 mol% and saponification ratio of 50 % or more is superior in both biodegradability and fluidity.

[0019]

As a fluidity improvement agent, further thermoplastic resin may be added which may be polyolefin, vinylpolymer, polystyrene, polyacrylonitrile, polyacetal, thermoplastic polycondensation produdct, thermoplastic polyimide, polyethylene, polypropylene, polyisobutylene, polyvinyl chloride, polyvinyl acetate, polystyrene, polyamide, polyester, polyure thane, polycarbonate, polyalkylenterephthalate, alkylene/vinylester copolymer, alkylene/acrylate or methacrylate copolymer, ABS copolymer, styrene/acrylonitrile copolymer, amide ether/amide ester block copolymer, ethylene vinyl acetate copolymer (EVA), ethylene/acrylate copolymer (EAA), ethylene/ethyl acrylate copolymer(EEA), ethylene/methacrylate copolymer (EMA), styrene/acrylonitrile copolymer (SAN), ethylene/maleic anhydride copolymer, amide ether/amide ester block copolymer, and urethane ether/urethane ester block copolymer. Moreover, such themoplastic resins easily become biodegradable themoplastic resin owing to its low molecular weight.

[0020]

To the composition of the present invention, filler, lubricant, mold release agent, plasticizer, foaming agent, stabilizer, extender, modifier, flow accelerator, colorant, and pigment may be added depending on necessity. Preferred lubricant is glycerin and stearic acid.

[0021]

The easily degradable molding of the present invention is covered with an anti-fungi agent facing at the molding surface of the above-described composition. The coating amount of the anti-fungi agent of the surface of the molding is preferably 2-40 $\mu g/cm^2$. The anti-fungi agent is preferably food preserver such as sorbic acid, sorbic acid salt, e-polylysine, allylisothiocyanate but other toxic anti-fungi agent such as phenols, metal salt of naphtenic acid,

salicylanilide. For food container, food preservatives are only allowable.

[0022]

Examples of food preservatives used in the present invention include sorbic acid, potassium sorbate, benzoic acid, sodium benzoate, potassium benzoate, propionic acid, calcium propionate, isobutyl paraoxybenzoate, butyl paraoxybenzoate, propyl paraoxybenzoate, dehydroacetic acid, sodium dehydroacatate, orthophenylphenol, orthophenylphenol salt, thiabendazol, diphenyl glycin, acetic acid, acetate, lactic acid, citric acid, adipic acid, alcohol, sodium nitrite, ε-polylysine, ethanol, storax extract, wormwood extract, "sirakon" protein, Japanese cypress thiol extract, decomposed pectin product from galacturic acid, extract from forsythia, fig leaf extract, oregano extract consisting of fatty acid and the flavonol, licorice extract consisting of flavonol, "grove" extract consisting of eugenol, sycamine extract consisting of stilbene derivative, koji acid, lamiaceae extract, cinnamon extract, ginger extract consisting of gingeol and gingerol, sage extract consisting of "sioneiru" and "kanfa", dock extract consisting of polygodial, tea extract consisting of catechin, raw soybean extract, garlic extract, bayberry extract consisting of eugenol and mochiiru, grape rind extract consisting of polyphenol, "propolis" extract consisting of flavonol, decomposed pink koji consisting of peptide, pepa extract consisting of binen, "hokkoshi" extract consisting of "bakuchioru", bamboo extract, rice hull extract, elysozyme, rosemary extract consisting of "rosemanol" or carvacrol, horseradish extract consisting of allylisothiocyanate, jujube extract, mace extract, mint extract, eucalyptus extract, the parsley extract, "majuramu" extract, thyme extract, coriander extract, bamboo grass frass extract, caraway extract, dale extract, anise extract, onion extract, "grove" extract, oregano extract, savory extract, cumin extract, thyme extract, caraway extract, protamin, chitosan, melanoidin, agar oligosaccharide, betaine, two ore more combination of them, gluconic acid, tartaric acid, lactic acid, glycine, phytin acid, polymeric phosphoric acid, malic acid, phosphoric acid, "tainin" acid, gallic acid, fatty acid, the ellagic acid, koji acid et cetera for control of pH.

[0023]

The method for forming the easily degradable molding from the composition of the present invention may contain, though not restrictive, injection molding, extrusion molding, inflation film molding, deflation film molding, T-die film molding, monofilament extrusion, melt fiber molding, T-die extrusion sheet molding, coat/hanger die extrusion sheet molding, extrusion flow molding, extrusion pipe molding, injection blow molding, sheet blow molding, stretching blow molding, multiple layer blow molding, direct vacuum molding, drape vacuum molding, air-lip molding, plug assisted vacuum molding, air cushion

vacuum molding, pressure molding, male/female die molding, slip molding, extrusion profile molding, extrusion foaming method, extraction coating molding, calendaring sheet forming, calendaring film forming, calendaring laser forming, press molding, transfer molding etc.

[0024]

The process of producing the easily degradable molding according to the present invention is characterized by kneading and molding the above described composition and then coating the surface of the resulting molding with anti-fungi agent. The method of coating of the anti-fungi agent may be direct coating and or by applying it on a mold or roll and then transferring therefrom. The transfer is preferred because the composition is heat-sterilized in molten condition and then molded in a mold having a coating of the anti-fungi agent and thus reduced fungi deposit on the surface of the molding, which shows a good storage life can be obtained.

[0025]

Further, the anti-fungi agent can be uniformly applied from a solvent such as aqueous ethanol solution in which the anti-fungi agent is dissolved. The pH of the aqueous solution is preferably pH 3-8, more preferably pH 4-7. This pH range does not erode the mold and at the same time has anti-fungi function. The method of transferring a food preservative using a mold is a method of applying the food preservative to the mold by spraying or brushing, and putting the easy degradable composition into the mold to obtain an easily degradable molding with the surface being exclusively covered with the food preservative. Cited as method of using a mold, are injection molding method, extrusive blow mold - blow method, extrusion blow method, sheet blow method, stretching blow method, multilayer blow method, direct vacuum blow method, a drape vacuum blow method, an air-lip vacuum blow method, a plug assist vacuum blow method, an air- cushion vacuum blow method, a compressed blow method, a male female blow method, a slip blow method, an extrusive profile blow method, an extrusive foaming method, a compressed blow method and a transfer blow method.

[0026]

The transfer method in the extrusion molding is a method of transferring anti-fungi agent to the surface of molding from a contact roll while the molding is being extruded. There are a method of dipping a molding into a container in which the anti-fungi agent is contained, and a method of spraying or brushing anti-fungi agent medicine onto a roll and contacting the molding with this roll to obtain a molding covered with the anti-fungi agent. As this kind of extrusion molding method, melted fiber spinning method, extrusion molding method, inflation film molding method, deflation film molding method and T die

extruding method, coat-hanger die film extrusion method, lamination method, monofilament extrusion molding method, compound monofilament extrusion molding method, melted fiber spinning method, T-die extruding sheet method, and extrusion coating method, calendaring film forming method, calendaring laser working method may be cited.

[0027]

In the following, the present invention will be explained in connection with examples which, however, show only a part of examples and the invention is not restricted to them.

[0028]

(Example 1)

Using 40mm single shaft extruder YE–40 (manufacturted by Yamaguchi Seisaku Sho) and a coat hanger die with a lip clearance of 1.2mm, a film of a composition consisting of 55.8 wt % of saponificated ethylene-vinylacetate-copolymer with 90% saponification ratio (specific gravity 1.27) from ethylene-vinylacetate copolymer containing 10 mol % ethylene, 6 wt% of water, 38 wt% of corn starch, 38 wt %, 0.1 wt% of titanium white, and 0.1 wt% of glycerine was obtained. The cylinder temperature was 130 ℃-146℃, and the die was 143 ℃. The screw revolution was 31 rpm, and the motor load current was 23A. The thickness of this film was fixed, and the surface of the film had no occurrence of the shark skin. Coating rubber rolls were dipped into a 70% ethanol aqueous solution containing 0.3% epsilon-polylysine (manufactured by Chisso K.K.) in a container and this solution was transferred from these rolls to both surfaces of the above-mentioned film, so that the final product has a film of a thickness of 35μg/cm^2. In addition, a film having no ε-polylysine was produced by not contacting the application roll. The film withdrawal speed was 17m/min and the thickness of the resulting film was 50 μm.

[0029]

To each one of the film of the two types produced, an aspergillus (black mold) suspension water was inoculated and cultured at 28℃ in an atmosphere of 90% humidity. As a result, during five days, on the film which was not covered with ε-polylysine, black mold emerged and the nature of easy degradability came to the fore. As for the film which was covered with ε-polylysine, no black mold was recognized at all even after duration of 60 days, and its commercial value was high. The surface of the film covered with ε-polylysine was wiped with wet dustcloth, and an aspergillus suspension water which is the black mold,

was inoculated and cultured at 28℃ in an atmosphere of 90% humidity in a manner similar to the procedure as mentioned. As a result, black mold emerged and nature of the easy degradablility by microbe came to the fore. The molding lost original shape after 25 day's decomposition in the compost. From this result, the easy degradable molding of this invention was superior in conservation, and after use was superior in the easy degradabiliy.

[0030]

(Example 2)

Using 50 mm diameter screw injection molding machine manufactured by Nissei Jushi Kogyo K.K. (maximum injection pressure is 1435kg/cm^2, FE160S25ASE A16M221), a composition consisting of 54.6 wt % of modified saponificated ethylene-vinylacetate-copolymer with 85% with partially saponified polyvinyl alcohol modified from ethylene-vinylacetate copolymer containing 22 mol % ethylene, 9 wt% of water, 38 wt% of potato starch and 0.6 wt% of talk, was injected according to the following conditions to obtain a molding. Injection timer is 22.0 seconds, cooling timer 20.0 is seconds, intermediate time timer is 5.0 seconds, measurement starting timer is 0.5 second, retract starting timer is 0.1 second, V5 fifth injection velocity is 15%, V4 fourth injection velocity is 15%, V3 tertiary injection velocity is 15%, V2 secondary injection velocity is 15% and V1 primary injection velocity is 15%, TP2 injection pressuring time is 20 seconds, S5 injection secondary pressure switching position15.0mm, S4 injection fifth velocity switching position 0.1mm, S3 injection fourth velocity switching position 20.0mm, S2 injection third velocity switching position 30.0mm, S1 injection secondary velocity switching position 60.0mm, SM measurement stop position 130mm, SD decompression position 2.0mm, P3 injection third pressure 1%, P2 injection secondary pressure 27%, P3 injection primary pressure 45%, over-packing prevention timer 0.1 second, injection breed OFF, VS screw rotation speed setting device 17%, screw back pressure setting device 1%, screw rotation switching is high, heating temperatures are 150H1, 156H1, 151 H2, 132 H3 and the mold temperature is 27℃.

[0031]

A aqueous 70% ethanol solution containing a 0.3% sodium sorbate (manufactured by Chisso K.K) which had been adjusted to pH 5 with gluconic acid was sprayed to inner surfaces of a pair of mold halves, and the above-mentioned commercial starch polymer-containing composition was injected, whereby a tray container having a transferred coating of 38μg/cm^2 of food preservative coated on the surface was prepared. Also, molding having no

food preservative coated thereon was prepared. The two types of containers were respectively inoculated with a suspension water of aspergillus which is black mold and cultured at 28℃ in an atmosphere of humidity 90%. As a result, during 5 days period, black mold appeared on the film which was not covered with ε-polylysine. As for the film which was covered with ε-polylysine, during 45 days period, no black mold not recognized at all and its commercial value was high. Thus, it was proved that potassium sorbate of Chisso K.K. has an anti-fungi function and a container of an easily degradable molding having excellent storage life.

[0032]

The surface of a tray container covered with a 0.3 % potassium sorbate adjusted to pH 5 with gluconic acid wiped thoroughly with water wetted cloth, and then inoculated with a water suspension of aspergillus and cultured at 28℃ at a atmosphere of 90% humidity. As a result, black mold appeared on the tray container which had not been covered with the potassium sorbate during 3 days period, the result being similar to that in which the molding was not covered with sorbate.

[0033]

(Example 3)

Example 3 was repeated to produce a tray container except that an aqueous ethanol solution of potassium sorbate was not adjusted from pH 8. The two types of containers were respectively inoculated with a suspension water of aspergillus which is black mold and cultured at 28℃ in an atmosphere of humidity 90%. As a result, black mold appeared during 3 days period on the tray container which was not covered with potassium sorbate, while black mold appeared during 5 days period. Thus, it was proven that the aqueous ethanol solution of potassium sorbate of pH 8 has weak anti-fungi action and a tray container comprised of an easily degradable resin exhibitis a superior storage life.

A tray container molding composed of an easily degradable resin having a superior storage life should be manufactured by utilizing potassium sorbate whose pH has been adjusted to acidic side with an organic salt.

[0034]

A tray container covered with potassium sorbate was wiping out from the surface with water wetted cloth, then inoculated with an aqueous suspension of aspergillus which is black mold, and cultured at 28℃ in an atmosphere of 90%

humidity. Black mold appeared within 3 days and the easily degradable nature with micro organism was reappeared.

[0035]

(Example 4)

A double screw having a screw compression ration of 1.03, L/D=25 and a Madoc at the tip was incorporated into 40mm single shaft extruder YE–40 (manufactured by Yamaguchi Seisaku Sho) , in which screen pack was removed and only a breaker was retained. Through a T-die having lip clearance 1.0 mm and 350 mm in width, a composition consisting of 65 wt % of ethylene-vinylacetate-copolymer with 35% partial saponificated vinylacetate containing 20 mol % ethylene, 13 wt% of water, 12 wt% of corn starch and 8 wt% of glycerin, was extruded into a sheet having a thickness of 80 μm at the cylinder temperature of 130℃-150℃ with screw revolutions of 72 rpm. The motor load was 37A and the resin pressure was 80kg/cm^2.

[0036]

A pudding cup mold was set on a vacuum working machine (FVF machine: manufactured by Fuse Vacuum Koki) and an aqueous ethanol solution of 0.3% sorbic acid adjusted to pH 5 with vinegar was sprayed on the inner surfaces of both mold halves and pudding cups were vacuum molded on the following vacuum molding conditions to produce a cup molding covered with a food preservative. Heating temperature was 31.0℃, molding cycle was 68-47 seconds, mold temperature was room temperature, pressure was 4kg/cm^2, mold closing pressure was 50kg/cm^2, upper heater was 13 seconds, lower heater was 32-13 seconds, molding delay was 0.1 second, molding time difference was 1 second, blow delay 0.2 second, blow vacuum 0.5 second, plug elevation was 0.3 second, vacuum delay was 0.1 second, vacuum cooling was 33 seconds, press delay 0.1 second, air pressing was 6 seconds, cooling delay was 10 seconds, cooling fan was 0.1 second, cooling spray 1 second, extended cooling was 1 second and release blow was 0.1 second.

[0037]

Further, pudding cups were also produced which did not have a coating of food preservative. These two types of pudding cups were inoculated with an aqueous suspension of aspergillus which is black mold and cultured at 28℃ at 90 % humidity. As a result, during 3 days black mold emerged on the pudding cup which was not covered with sorbic acid, while no black mold appears on the pudding cup even after 50 days. This result proves that the sorbic acid has anti-fungi action and thus excellent vacuum molding which has a superior

storage life was produced. After wiping out with wet cloth the film surface which had been covered with sorbic acid, the film was inoculated with aspergillus and cultured at 28℃ in an atmosphere of 90% humidity and a black mold appeared during 3 days which was the same as film which was not covered with sorbic acid and thus the easily degradable nature by microorganisms appeared again.

[0038]

(Example 5)

Extruder Type D-90 single shaft D-90 extruder air-cooled inflation machine (manufactured by Modern Machinery Co., Ltd) having a screw provided with a central Madock was used, in which a single 40 mesh screen pack was inserted and a first pinch roller was actuated under 2 kg/cm^2, to form an inflation film from a composition consisting of 56 wt % of ethylene-vinylacetate-copolymer with 78% partial saponificated vinylacetate containing 55 mol % ethylene, 2 wt% of water, 37 wt% of wheat starch and 5 wt% of glycerin. The cylinder temperature was between 115℃ and 150℃, the die temperature was 140℃, the screw revolution was 15 rpm, and the motor load was 150 A. The film withdrawing speed was 65/min and the thickness of the product film was 50 μm.

[0039]

Allylisothiocyanate was transferred by a process of dipping application rolls in a ethanol solution containing 0.3% of allylisothiocyanate (manufactured by Midori Juji) contained in a vessel and contacting the rolls to the film from both surfaces of the film, to obtain a final product having a coating of 10μg/cm^2. Also, a film not covered by allylisothiocyanate was produced. The film drawing velocity was 65m/min and the film thickness was 50μm.

The two type of films produced were respectively inoculated with an aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity. As a result, black mold appeared during 3 day period on the film which was not covered with allylisothiocyanate while no black mold was recognized even after lapse of 7 days. This result proves that allylisothiocyanate has anti-fungi function and produced an easily degradable film molding having an excellent storage life.

After wiping out the film covered with the 0.3% allylisothiocyanate (manufactured by Midori Juji) with a water-wetted cloth, the film was inoculated with an aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity. As a result, black mold

appeared during 3 day period on the film which was the same as the result with the film not covered with allylisothiocyanate and thus the easily degradable nature reappeared.

[0040]

(Example 6)

A film not covered with food preservative of Example 5 was left in a polyethylene bag containing a volatile allylisothiocyanate. This film and another film on which allylisothiocyanate was coated were inoculated with aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity. As a result, no black mold appeared at all even after lapse of 6 days. With the film not covered with allylisothiocyanate, black mold appeared during 3 days. From this result, it is proved that allylisothiocyanate has anti-fungi action and produced an easily degradable resin film molding having an excellent storage life. However, the films of Examples 5 and 6 had strong odor of horseradish and thus the easily degradable resin film molding are unfortunately restricted in its application. The sheet coated with allylisothiocyanate was taken out of the polyethylene bag, left in the air until the horseradish odor disappeared, inoculated with an aspergillus suspension and cultured at 28 ℃ in an atmosphere of 90 % humidity. Black mold appeared during 3 day period and this result is the same as the film not covered with allylisothiocyanate and thus the easily degradable nature by microorganism reappeared.

[0041]

(Example 7)

YE-40 single shaft extruder (manufactured by Yamaguchi Seisakujo) and MBM monofilament stretcher, with the screw compression ratio of 1.03, L/D=25, small compression part pitch and Madock end, in which a 40 mesh single stainless steel screen pack was inserted, were used to produce a monofilament having a stretching ratio of more than 10% from a composition consisting of 57.9 wt % of modified ethylene-vinylacetate-copolymer with 15% partial saponification containing 7 mol % ethylene, 14 wt% of water, 28 wt% of wheat starch and 0.1 wt% of glycerin. The cylinder temperature was between 127℃ and 150℃, the die temperature was 145℃, the screw revolution was 58 rpm, and the motor load was 21 A.

From a pair of application rolls (kiss rolls) dipped in an aqueous 70% ethanol solution of 0.3% ε-polylysine (manufactured by Chisso K.K.) contained in a container, the solution was transferred to the opposite surface areas of the

monofilament to form a coating of the final product of 28μg/cm². In addition, a monofilament was produced without ε-polylysine coating. The withdrawal velocity was 37m/min and the resulting filaments had 80 denier.

[0042]

(Example 8)

The resulting two type monofilaments were respectively inoculated with aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity for one day, and replicated in a food stamp for Eumycetes (sold by Chisso K.K.) and cultured at 28℃ in an atmosphere of 90% humidity for 3 days. On the monofilament not covered with ε-polylysine, a great number of colonies appeared, while no colony developed on the monofilament covered with ε-polylysine even after lapse of 10 days. From this fact, it is proved that ε-polylysine has anti-fungi action and produced a easily degradable plastic film molding with an excellent storage life. After wiping out the surface of the monofilament covered with e-polylysine with a water-wetted cloth, the monofilament was inoculated with aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity for one day, and replicated in a food stamp for Eumycetes (sold by Chisso K.K.) and cultured at 28℃ in an atmosphere of 90% humidity for 3 days and a great number of colonies were formed and the easily degradable nature with microorganism reappeared.

[0043]

(Example 8)

Extruder Type D-90 single shaft D-90 extruder air-cooled inflation machine (manufactured by Modern Machinery Co., Ltd) having a screw provided with a central Madock was used, in which a single 40 mesh screen pack was inserted and a first pinch roller was actuated under 2 kg/cm², to form an inflation film from a composition consisting of 15 wt% of ethylene-vinylacetate-copolymer with 95 % saponification containing 0.5 mol % ethylene, 21.9 wt% of corn starch containing18 wt% of water, 0.1 wt% of glycerin, and 45 wt% of polycaprolactone. The cylinder temperature was between 135℃ and 165℃, the die temperature was 170℃, the screw revolution was 25 rpm, and the motor load was 155 A. The film withdrawing speed was 40/min and the thickness of the product film was 65 μm.

[0044]

(Example 9)

Allylisothiocyanate was transferred by a process of dipping application rolls in a ethanol solution containing 0.3% of allylisothiocyanate (manufactured by Midori Juji) contained in a vessel and contacting the rolls to the film from both surfaces of the film, to obtain a final product having a coating of 10μg/m^2. Also, a film not covered by allylisothiocyanate was produced. The film drawing velocity was 20m/min and the film thickness was 60μm.

The two type of films produced were respectively inoculated with an aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity. As a result, black mold appeared during 3 day period on the film which was not covered with allylisothiocyanate, while no black mold was recognized at all even after lapse of 5 days. This result proves that allylisothiocyanate has anti-fungi function and produced an easily degradable film molding having an excellent storage life.

After wiping out the film covered with the 0.3% allylisothiocyanate (manufactured by Midori Juji) with a water-wetted cloth, the film was inoculated with an aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity. As a result, black mold appeared during 3 day period on the film which was the same as the result with the film not covered with allylisothiocyanate and thus the easily degradable nature reappeared.

[0045]

(Example 9)

YE-40 single shaft extruder (manufactured by Yamaguchi Seisakujo) and MBM monofilament stretcher, with the screw compression ratio of 1.03, L/D=25, small compression part pitch and Madock end, in which a 40 mesh single stainless steel screen pack was inserted, were used to produce a monofilament having a stretching ratio of more than 10% from a composition consisting of natural polymer (starch) called as Mater-Bi AF05H as easy biodegradable resin. The cylinder temperature was between 148℃ and 154℃, the die temperature was 155℃, the screw revolution was 58 rpm, and the motor load was 21 A.

From a pair of application rolls (kiss rolls) dipped in an aqueous 70% ethanol solution of 0.3% ε-polylysine (manufactured by Chisso K.K.) contained in a container, the solution was transferred to the opposite surface areas of the monofilament to form a coating of the final product of 28μg/cm^2. In addition, a

monofilament was produced without ε-polylysine coating from the rolles. The withdrawal velocity was 17m/min and the resulting filaments had 80 denier.

[0046]

The resulting two type monofilaments were respectively inoculated with aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity for 2 days, and replicated in a food stamp for Eumycetes (sold by Chisso K.K.) and cultured at 28℃ in an atmosphere of 90% humidity for 2 days. On the monofilament not covered with ε-polylysine, a great number of colonies appeared, while no colony grew on the monofilament covered with ε-polylysine even after lapse of 10 days. From this fact, it is proved that ε-polylysine has anti-fungi action and produced a easily degradable plastic film molding with an excellent storage life.

After wiping out the surface of the monofilament covered with e-polylysine with a water-wetted cloth, the monofilament was inoculated with aqueous suspension of aspergillus which is black mold and cultured at 28℃ in an atmosphere of 90% humidity for one day, and replicated in a food stamp for Eumycetes (sold by Chisso K.K.) and cultured at 28℃ in an atmosphere of 90% humidity for 3 days and a great number of colonies grew and the easily degradable nature with microorganism reappeared.

[0047]

(Example 10)

(Example 1)

Using 40mm single shaft extruder YE–40 (manufactured by Yamaguchi Seisaku Sho) and a coat hanger die with a lip clearance of 1.2mm, a film of a commercially available easily degradable resin containing a starch polymer called NOVON M4900 was obtained. The cylinder temperature was 134 ℃ -167℃□, and the die was 162 ℃. The screw revolution was 32 rpm, and the motor load current was 23A. Coating rubber rolls was dipped into a container in which a 70% ethanol aqueous solution containing 0.3% ε-polylysine (manufactured by Chisso K.K.) was contained, and this solution was transferred from the rolls to both surfaces of the above-mentioned film, so that the final product has a film of a thickness of 37μg/cm^2. In addition, a film having no ε-polylysine was produced by not contacting the application rubber rolls. The film withdrawal speed was 35m/min and the thickness of the resulting film was

45 μm.

[0048]

To each one of the film of the two types produced, an aqueous suspension of aspergillus which is black mold was inoculated and cultured at 28℃ in an atmosphere of 90% humidity. As a result, during 3 day period, black mold emerged on the film which was not covered with ε-polylysine, and the nature of easy degradability came to the fore. As for the film which was covered with ε-polylysine, no black mold was recognized at all even after lapse of 60 days, and its commercial value was high.

The surface of the film covered with ε-polylysine was wiped out with wet cloth, and an aqueous suspension of aspergillus which is the black mold, was inoculated and cultured at 28℃ in an atmosphere of 90% humidity in a manner similar to the procedure as mentioned. As a result, black mold emerged during 3 days and nature of the easy degradablility by microbe came to the fore. From this result, the easy degradable molding of this invention has an excellent storage life and, after use, an excellent degradabiliy.

[0049]

(Comparative Example)

Among the examples, easily degradable resins on which food preservatives were not coated by the transfer method and which developed black mold are comparative examples.

[0050]

The easily degradable moldings according to the present invention were easily molded, had stable dimensions, and were capable of being commercially molded. Also, the easily degradable moldings according to the present invention suppressed development of fungi under accelerated test conditions of cultivation at 28℃ at 90% humidity, and after wiping the moldings after their use, the biodegradable activity was accelerated and thus the moldings decayed. The easily degradable moldings which used plastic resins comprised of a starch polymer, water and biodegradable thermoplastic resin, showed good biodegrading properties. Particularly, saponificated ethylene-vinylacetate-copolymer and polycaprolactone exhibited good biodegradability. The easily degradable molding which was a composition containing 2-15 wt% of water had excellent molding properties and fluidity, and good outer appearance. The easily degradable moldings which used modified starch such as chemically modified starch, chemically decomposed starch, oxygen modified starch and physically modified starch from raw starch had good appearance and excellent

biodegradation.

[0051]

The method of applying an aqueous solution of anti-fungi agent having pH 3-pH 8 did not corrode the molds and gave a good anti-fungi property. The method of applying anti-fungi agent to molds or rolls and then transferring the agent to the molding is superior because the surfaces are coated with anti-fungi agent with least contamination, and thus processing of moldings without bringing contaminants into the moldings and a long storage line is made possible. And thus the easily degradable moldings bring superior effects to both industry and environment and accordingly can be widely adopted in the industry.